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Inertization Effects on the Explosion Parameters of Different Mix Ratios of Ethanol and Toluene – Experimental Studies

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Abstract: *Each flammable substance has a range in which it can be explosively ignited when mixed with air at given temperatures and pressures. For fire or explosion to occur the appropriate amounts of oxidant and flammable substance are necessary at a concentration at least equal to its lower explosive limit. High potential toxicity and flammability of mixtures used in industry can lead to serious harm to people and the environment. Therefore, preventing accidents which can result in fire and/or explosion, is an important factor in the design of chemical processes. For this purpose, a process called inertization can be applied. In this paper the explosion characteristics of mixtures of two solvents: ethanol-toluene is discussed. Explosion parameters were experimentally determined using a closed vessel of 20 l at 120 °C and ambient pressure. Results are shown graphically as ternary diagrams with the explosion hazard areas highlighted. Results show importance of inertization in process safety.*

Keywords: *explosion limits, lower explosion limit (LEL), upper explosion limit (UEL), limiting oxygen concentration (LOC), limiting air concentration (LAC)*

1. Introduction

Each flammable gas or flammable vapour when mixed with air under appropriate conditions, can form an explosive atmosphere. In order to prevent the occurrence of such an atmosphere one must accurately identify potential threats [1]. By analyzing these factors, and identifying potential threats, it is possible to assess whether an explosive atmosphere can be created in the first place. If there is the possibility of fire/explosion, a risk assessment has to be conducted. The risk assessment includes possible effects of an explosion and their minimization. How can the hazard of an explosive atmosphere be minimised? One of the most common methods is through inertization; in other words, the partial or complete replacement of air in a flammable atmosphere with an inert gas. When working with explosive mixtures the limiting oxygen concentration should be determined. Experimentally, the inertization process is examined by determination of the limiting oxygen concentration. Examples of inert gases which decrease the concentration of an oxidant in a flammable mixture are carbon dioxide, argon and nitrogen.

Explosion parameters include: Lower and Upper Explosion Limits (*LEL* and *UEL*), Limiting Oxygen Concentration (*LOC*), Limiting Air Concentration (*LAC*), maximum explosion pressure (p_{max}) and maximum rate of pressure rise ($(dp/dt)_{max}$). These parameters can be determined experimentally or estimated. In this article the *LEL*, *UEL*, *LOC* are discussed.

LEL, UEL:

In the past, many explosion properties have been studied using different research methods. One of these is based on reaction stoichiometry, equations (1), (2) and (3) [2].

$$C_mH_xO_y + zO_2 \rightarrow mCO_2 + \frac{x}{2}H_2O \quad (1)$$

$$z = m + \frac{x}{4} - \frac{y}{2} \quad (2)$$

$$C_{st} = \frac{1}{1+\frac{z}{0,21}} \quad (3)$$

where C_{st} is % volume of flammable substance in air.

Another method is correlating explosion limits and the heats of combustion. This method was used for organic compounds containing carbon, hydrogen, oxygen, nitrogen and sulfur. The correlation is shown as equations (4) and (5) [2].

$$LEL = -\frac{3.42}{\Delta H_c} + 0.569\Delta H_c + 0.0538\Delta H_c^2 + 1.20 \quad (4)$$

UEL = 6.30ΔHc + 0.567ΔHc22 + 23.5 (5)

where *LEL* and *UEL* are % volume of flammable substance in air and ΔH_c is in 10^3 kJ/mol.

<u>*LOC:*</u>

LOC is defined as a maximum oxygen concentration of flammable substance in air, at which there is not observed an explosion of the mixture. *LOC* depends highly on the kind of the inert gas. Its value, as with the value of the explosion limits, is also affected by the process conditions, namely temperature and pressure. *LOC* can be calculated using the following formula (6) [3].

$$LOC = z \cdot LEL \quad (6)$$

LOC is expressed in mole or percentage volume of oxygen in the mixture.

In this paper, results of the experimental studies of the explosion parameters and the effect of inert gas on the explosion range of ethanol-toluene mixtures are described. This knowledge of the explosion parameters is very important in designing equipment in industrial processes and in the explosion risk analysis. Organic solvents are the most common source of fires and explosions and these are widely used in chemical processes [4]. To perform a risk analysis, one should be thoroughly familiar with the explosive characteristics of the substance. Because of the importance of these parameters, the values should be included in each MSDS and safety report. According to CLP Regulations [5] both the solvents under discussion are flammable liquids. Their flash points are below 23 °C and the initial boiling points are above 35 °C. Hence, ethanol and toluene are in Category 2, according to CLP Regulations.

2. Experimental apparatus and method

The experiments were performed in a closed, spherical, stainless steel test vessel of 20 litre internal volume (known as the 20 l Spherical Explosion Vessel). It was designed and constructed by the ANKO company and the Institute of Industrial Organic Chemistry. It includes pressure and temperature sensors, vacuum pump, heating system, stirrer and data logger. The data logger transmission interface was established for recording the explosion pressure – time records. The vessel and ancillary equipment is shown in Fig. 1. Using this vessel, it is possible to measure explosion pressures up to 16 bar and to work at temperatures up to 150 °C. The ignition source is a fusing wire, placed at the center of the test vessel. This releases between 10 J – 20 J of energy. The vessel was set up in accordance with the relevant European standard [6].

<u>*LOC determination – procedure:*</u>

This begins with the production of a mixture containing the tested substance, air and inert gas. According to the European standard, the determination is carried out using the PN-EN 14756 standard [3]. To determine the *LOC*, two methods are recommended: method T and method B, which are described in detail in PN-EN 1839 [6]. The two standards, PN-EN 14756 and PN-EN 1839 are strongly interdependent. Without PN-EN 1839 standard it is not possible to determine the *LOC*. This paper presents the test results obtained using method B also known as the bomb method. *LOC* is calculated from the *LAC* value. The formula describing this relationship is (7) [3]:

$$LOC = 0.209 \cdot LAC \quad (7)$$

Determination of the *LAC* start of the appointment of the apex of the explosion area. To do this, the *LEL* and *UEL* must first be determined in accordance with PN-EN 1839. Next, the explosive limit with the mole fraction of the test substance $x_{TS} = 1.2LEL$ and variable percentage of air and inert gas is determined. After that, the area around the apex of the explosion area should be investigated by carrying out ignition attempts and changing the amount of the test substance and the constant mole fraction of air (x_{AIR}). Then, the explosion limits should be determined at $0.8x_{IN}$. These confirm that the *LAC* is at the apex of the explosion area. Thus, the determination of the *LOC* is complete.

Figure 1. 20 l spherical explosion vessel

The testing was carried out in several steps. To start, the pressure in the test vessel was reduced to below10 mbar. At this pressure, the sample was injected into the vessel. Than nitrogen was added into the vessel up to required pressure. After injection of the sample and required amount of nitrogen, air was injected until atmospheric pressure was obtained in the vessel. The mixture in the vessel was then stirred for 3 min. The gaseous mixture was allowed to stabilize without stirring for 3 min. It was ignited and the data from the pressure sensor were processed by the computer. After the explosion, the vessel was purged with air, opened and cleaned.
The aim of this work was to determine the experimental explosion characteristics. The tests for ethanol – toluene mixes at different ratios were carried out at ambient pressure. An optimal temperature of 120 °C was selected for all of the mix analyzed, thereby ensuring that both solvents were in the vapour state during ignition.

3. Results and Discussion

First step of the research was to determine the explosion limits for the various mixes. The results are shown in Table 1. It can be seen that ethanol has got the wider explosion range while that of toluene is narrower. The explosion ranges vary depending on the content of ethanol and toluene.

Table 1. Explosion limits for ethanol – toluene mixes in different ratios

Explosion limits	Mixture: ethanol : toluene [mol%]				
	100:0	**70:30**	**50:50**	**30:70**	**0:100**
LEL [mol%]	2.6	1.7	1.4	1.1	0.8
UEL [mol%]	22.0	17.8	12.6	10.4	7.6

Knowing the explosion limits, determination of the *LOC* was started. Firstly, the tests were conducted at $x_{TS} = 1.2LEL$. Then the inert fraction (x_{IN}) and the air fraction (x_{AIR}) were obtained. With the higher concentration of nitrogen in the mixture, the lower explosion pressure and the lower explosion pressure rise were obtained. The area around the explosion apex was determined by carrying out the tests at concentrations higher by 0.2 mol% and lower by 0.2 mol% than x_{TS}. The obtained pressure values were lower than the criterion value of 0.06 bar which confirmed the correct determination of the apex. After that, the explosion limits were determined at $0.8x_{IN}$. All results are presented and compared in Table 2 and are illustrated in the ternary diagrams (Figures 2 – 6).

Table 2. Limiting oxygen concentration – determination results

Substance or mixture / parameter	1.2*LEL*	x_{IN}	x_{AIR}	$0.8x_{IN}$	
				LEL	*UEL*
	[mol%]				
Ethanol	3.20	50.50	46.30	3.2	10.7
Ethanol 70 mol% – Toluene 30 mol%	2.04	60.50	37.46	1.8	4.6
Ethanol 50 mol% – Toluene 50 mol%	1.68	60.50	37.82	1.3	4.3
Ethanol 30 mol% – Toluene 70 mol%	1.32	60.50	38.18	0.9	4.4
Toluene	0.96	60.50	38.54	0.8	3.3

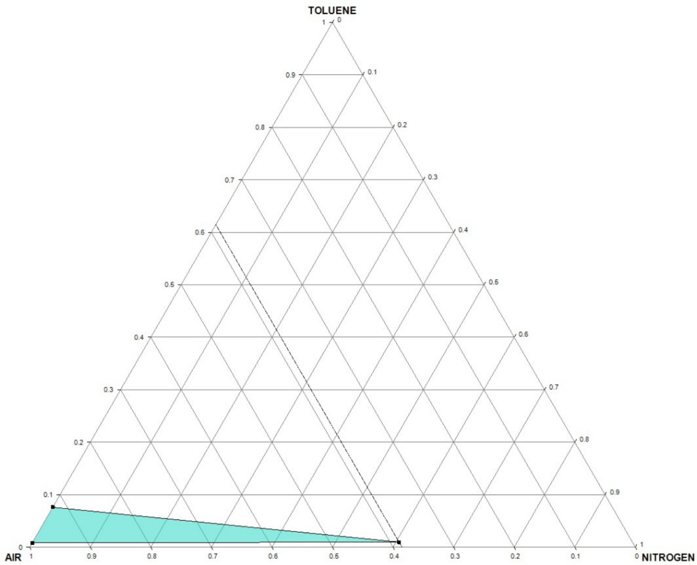

Figure 2. Ternary diagram for toluene

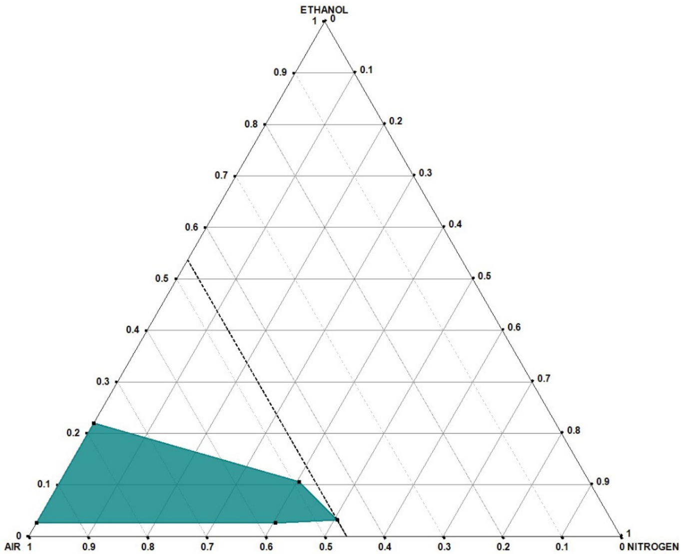

Figure 3. Ternary diagram for ethanol

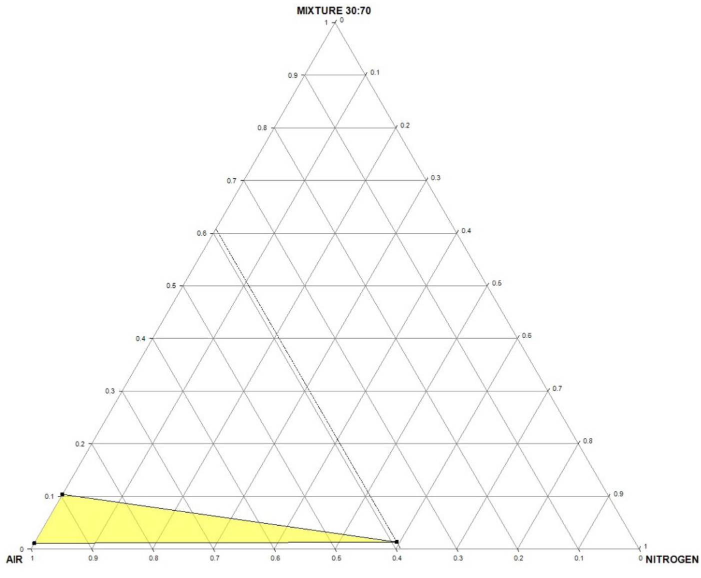

Figure 4. Ternary diagram for mixture of ethanol 30 mol% : toluene 70 mol%

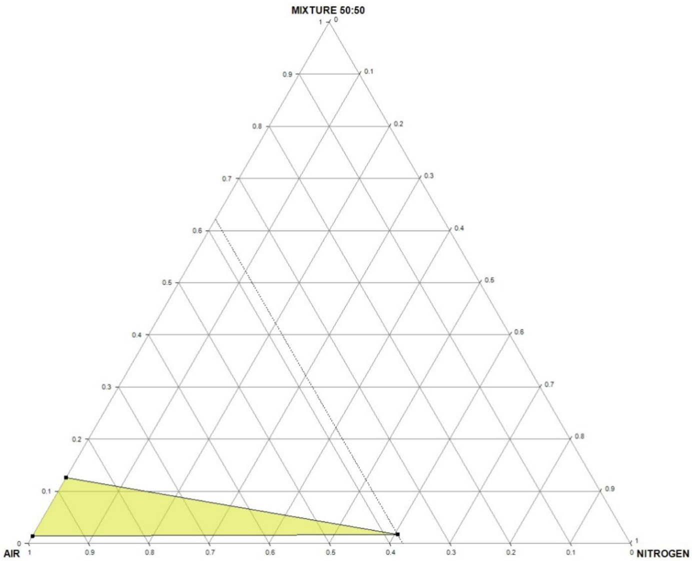

Figure 5. Ternary diagram for mixture of ethanol 50 mol% : toluene 50 mol%

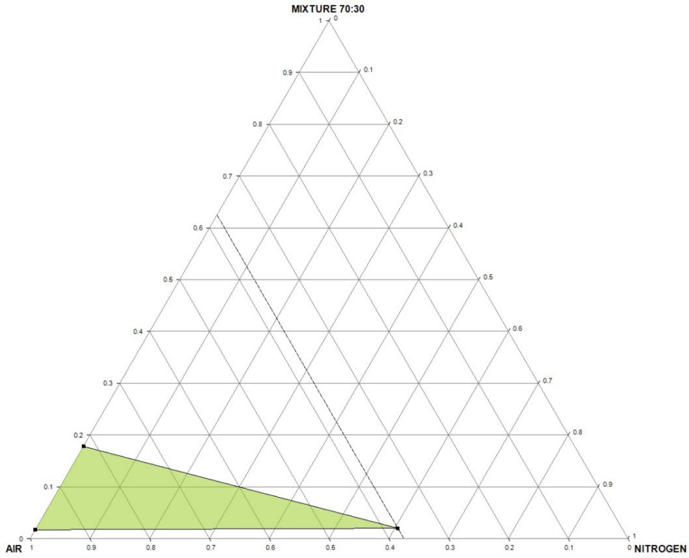

Figure 6. Ternary diagram for mixture of ethanol 70 mol% : toluene 30 mol%

The first and most important thing in determining *LOC* is the correct determination of the apex of the explosion area. Because in the studies of selected substances and mixtures the short procedure was used, the apex of the explosion area determined the value of the *LOC* [7]. A tangent drawn to the apex determined the explosion area. Thus, the *LAC* could be read and then on this basis the *LOC* might be calculated. In Table 3 the values of the *LAC* are compiled with the corresponding values of the *LOC*. As can be seen, ethanol yielded the highest *LAC* and *LOC*. With an increase in the toluene content in a mixture with ethanol, the values decreased. It is interesting that in the case of ethanol 70 mol% - 30 mol% toluene and ethanol 50 mole% - 50 mole% toluene these values are similar. The values for ethanol 70 mole% - 30 mole% of toluene are actually equal to the values for toluene. It can be concluded that the high content of toluene in the mixture results in the *LAC* and the *LOC* of the mixture and pure toluene being the same.

Table 3. Comparison of *LAC* and *LOC* values for ethanol - toluene mixes

Substance or mixture / parameter	*LAC* [mol%]	*LOC* [mol%]
Ethanol	46.3	9.7
Ethanol 70 mol% – Toluene 30 mol%	37.5	7.8
Ethanol 50 mol% – Toluene 50 mol%	37.8	7.9
Ethanol 30 mol% – Toluene 70 mol%	38.2	8.0
Toluene	38.5	8.0

4. Conclusions

Ethanol with toluene is a good combination of solvents due to the formation of an azeotrope. Mixtures of organic solvents are a common source of fires and explosions, which is why this research was undertaken, to model the mixtures of ethanol with toluene and determine their explosive properties. Results of these studies have confirmed that increases of toluene in the mix decreases the molar fraction of the test substance which results in a narrowing of the explosion limits and the entire explosion area. Considering only the results of the *LOC* determinations, the mixture of ethanol and toluene in ratios 30:70 [%mol/mol] is the least hazardous. Also, by analyzing the explosion parameters and the ternary diagram, this mixture exhibited the narrowest explosion area. At the largest mole fraction of ethanol in the mixture, the value of the *LOC* is greatly diminished, even to values lower than the *LOC* of toluene. Because mixtures of organic solvents are very common in industry, results of these tests can be applied to industrial processes in order to make them safer for people and the environment. These experiments can be a prelude to further research in the field of explosive vapours.

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